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Inventor: UCHIDA TSUTOMU; IKEDA IKUKO; OMURA AKIRA; TSUDA SAKAE; MIURA KAZUNORI; EBINUMA TAKAO

Applicant: NAT INST OF ADV IND & TECHNOL

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#### Abstract of JP2005089353

PROBLEM TO BE SOLVED: To provide a method for suppressing the formation of a clathrate compound form water and gas and/or liquid such as a solvent.

SOLUTION: The method for suppressing the formation of the clathrate compound comprises adding a globular type III antifreeze protein when the clathrate compound is formed from water and gas and/or liquid such as a solvent. The method for conveying and storing gas and/or liquid using the suppressing method is also provided. The method for preventing clogging of transporting pipes for gas and/or liquid by the clathrate compound using the suppressing method is also provided.

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3. In the drawings, any words are not translated.

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## CLAIMS

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[Claim(s)]

[Claim 1]

The formation control approach of the clathrate compound which controls formation of this clathrate compound by a clathrate compound's facing being formed from liquids, such as water, atmosphere, and/or a solvent, and adding the spherical non-\*\* protein of Type III.

[Claim 2]

The formation control approach according to claim 1 that atmosphere is rare gas, such as sour gases, such as hydrocarbon gas, such as methane and a propane, carbon dioxide gas, and a hydrogen sulfide, and neon, and a krypton.

[Claim 3]

The formation control approach according to claim 1 that liquids are organic solvents, such as fluorocarbon, such as HFC-32 and HFC-134a, a tetrahydrofuran, and an acetone, or organic solvents which form a clathrate compound under coexistence with atmosphere according to claim 2, such as a methylcyclohexane and an isopentane, and liquid hydrocarbon.

[Claim 4]

Transportation and the storage condition of the atmosphere and/or the liquid which are characterized by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound in case liquids, such as atmosphere and/or a solvent, are conveyed and stored.

[Claim 5]

Transportation and the storage condition of the atmosphere according to claim 4 and/or the liquid whose atmosphere is rare gas, such as sour gases, such as hydrocarbon gas, such as methane and a propane, carbon dioxide gas, and a hydrogen sulfide, and neon, and a krypton, etc.

[Claim 6]

Transportation and the storage condition of the atmosphere according to claim 4 and/or the liquid whose liquids are organic solvents, such as fluorocarbon, such as HFC-32 and HFC-134a, a tetrahydrofuran, and an acetone, or organic solvents which generate a clathrate compound under coexistence with atmosphere according to claim 5, such as a methylcyclohexane and an isopentane, and liquid hydrocarbon.

[Claim 7]

How to prevent lock out of a duct by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound in the approach a duct conveys liquids, such as atmosphere and/or a solvent.

[Claim 8]

How to prevent lock out of the duct according to claim 7 whose atmosphere is rare gas, such as sour gases, such as hydrocarbon gas, such as methane and a propane, carbon dioxide gas, and a hydrogen sulfide, and neon, and a krypton.

[Claim 9]

The approach a liquid prevents lock out of the duct according to claim 7 which are organic solvents, such as fluorocarbon, such as HFC-32 and HFC-134a, a tetrahydrofuran, and an acetone, or organic

solvents which generate a clathrate compound under coexistence with atmosphere according to claim 5, such as a methylcyclohexane and an isopentane, and liquid hydrocarbon.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [Field of the Invention]

[0001]

This invention relates to the approach of controlling a generation process by generating in a duct, in case petroleum and natural gas are conveyed, and dissolving the spherical non-\*\* protein of Type III into a water solution, in order to control generation of the clathrate compound used as the cause of causing lock out accident.

#### [Background of the Invention]

[0002]

A molecule (it is called a guest molecule) and water (called a host molecule), such as hydrophobic gases, such as natural gas, and a solvent like fluorocarbon and a tetrahydrofuran, react under low-temperature high-pressure conditions, and a clathrate compound tells the high concentration far exceeding the solubility to water (or ice) the thing of the solid-state which involved the guest molecule. Although this matter was discovered at the end of the 18th century, the accident which a transportation pipe will blockade in the petrochemical plant of a high latitude area in the 1950s arose, and it attracted attention greatly as this causative agent. In order to prevent such accident after that, research has been advanced focusing on the technique which checks generation (see the nonpatent literature 1).

[0003]

A clathrate compound mainly takes two kinds of crystal structures. It is the I-beam crystal (a cubic, about 1.2nm of unit-cell length) which one reacts with methane, carbon dioxide gas, etc., and is generated, and another is II mold crystal (a cubic, about 1.7nm of unit-cell length) which reacts with a tetrahydrofuran, a liquefied petroleum gas, etc., and is generated. Although it consists of a grid from which a water molecule makes all, an icy crystal (hexagonal,  $a = 0.45\text{nm}$  of unit-cell length,  $c = 0.74\text{nm}$ ) is different structure, and water intermolecular distance also differs, respectively.

[0004]

Current serves as a candidate for research as a technique in which current and the generation control technique of a clathrate compound which the fossil fuel develops in polar regions and a large depth-sounding area gradually are old, and it is new (for example, nonpatent literature 2 reference).

Moreover, all over the submarine deposit and the permafrost layer of a polar region, it is known that the natural gas which is not only what accompanies such a fossil fuel is \*\*\*\*(ing) in the form of a clathrate compound, and the development research for developing these as a natural gas resource in recent years is started (see the nonpatent literature 3). Examination is beginning to be performed also about the technique which uses unique properties, such as high density guest molecule concealment nature which a clathrate compound furthermore has, and guest molecule selectivity at the time of generation and a decomposition reaction, and is used industrially. for example, as separation technology using a clathrate compound of mixed gas "Separation of the mixed gas using gas-hydrate and the freshening approach of seawater" (patent reference 1), the "isotope separation approach" (patent reference 2), the "separation approach of rare gas" (patent reference 3), etc. are reported.

Having the point that low energy nature, small facility nature, low environmental load nature, etc. were excellent compared with technique, such as the low-temperature-separation method and membrane-separation method for having used the boiling point difference of each component in the mixed gas currently performed from the former, and an oscillating adsorption separation method, is

known.

[0005]

In such ED, it is very important to control generation / decomposition behavior of a clathrate compound. As especially mentioned above, about the technique which controls generation of a clathrate compound, the application range is wide. Moreover, correlation is between the growth rate in a clathrate compound, and the guest molecule concentration in the formed clathrate compound, and in order to obtain a clathrate compound with the guest molecule concentration of a complement, it is necessary to control a generation rate.

[0006]

As a technique which controls generation of a clathrate compound, the approach using the two mainly following additives is in use. One is the approach of using the additives (for example, seawater, alcohol, etc.) shifted to an equilibrium condition of clathrate compound control-side, and it is the approach of using the additive (chemicals, such as PVP) which controls the crystal generated although other one did not change most equilibrium conditions. Although any approach is used in actual production, since the former additive does not necessarily control growth of a clathrate compound, if it becomes the equilibrium condition which the system shifted, generation of a clathrate compound cannot be controlled. Moreover, as for the latter additive, although development is furthered, effect evaluation to an environment etc. is not fully performed, but an economical problem also has current [ much ].

[0007]

Uchida et al. (nonpatent literature 4 (1999)) conducted the generation experiment of a carbon-dioxide-gas clathrate compound, and investigated the growth rate of the film-like clathrate compound generated by the pure-water-carbon-dioxide-gas interface. Consequently, it turned out that it is expressed with the function of the gap (whenever [ supercooling ] DT) from the terminal temperature of temperature in case the growth rate of a carbon-dioxide-gas clathrate compound starts generation under the pressure. Furthermore, the clathrate compound which Uchida et al. (2002) conducts the same experiment in the water solution containing NaCl, and is generated by the NaCl water-solution-carbon-dioxide-gas interface found out that growth rate depressor effect was so large that a growth rate's being slower than a pure-water system and NaCl concentration are high (nonpatent literature 5).

[0008]

As a generation control technique of the ice which is the same hydride system crystal as a clathrate compound, the use ED of the non-\*\* protein produced naturally in recent years is active. This non-\*\* protein adheres alternatively on the icy crystal face, and it is said that it has the work which controls that crystal growth. However, the function is limited to the icy crystal structure, and is evaluated.

[0009]

Zeng and others (nonpatent literature 6) pointed out possibility that the spiral non-\*\* protein classified into Type I would control generation of II mold clathrate compounds, such as tetrahydrofuran and a liquefied petroleum gas, recently. However, effect is taken only to II mold crystal structure, and there is no report about the effectiveness to the I-beam clathrate compound crystal which reacts with methane and carbon dioxide gas which are the principal component of natural gas, and is generated.

[0010]

[Patent reference 1] JP,11-319805,A

[Patent reference 2] JP,2000-33236,A

[Patent reference 3] JP,2000-107549,A

[Nonpatent literature 1] Sloan, E.D.Jr., Clathrate Hydrates of Natural Gases 2ndEd. Revised and Expanded, Marcel Dekker Inc., 1998

[Nonpatent literature 2] Carroll, J.J., Natural Gas Hydrates: A Guide for Engineers, Butterwort-

Heinemann, 2002

[Nonpatent literature 3] Paull, C.K and Dilloin, W.P. Eds., Natural Gas Hydrates: Occurrence, Distribution, and Detection

[Nonpatent literature 4] Uchida et al. J. Crystal Growth, 204, p. 348, 1999

[Nonpatent literature 5] Uchida et al. J. Crystal Growth, 237-239, p. 383, 2002

[Nonpatent literature 6] Zeng et al Can. J. Phys., 81, p.17, 2003

[Nonpatent literature 7] Sicheri et al. Nature, 375, p. 427, 1995

[Nonpatent literature 8] Gronwald et al. Biochemistry, 37, p. 4712, 1998

[Nonpatent literature 9] Jia et al. Nature, 384, p. 285, 1996

[Nonpatent literature 10] Deng et al. Biochim. Biophys. Acta, 1388, p.305, 1998

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0011]

this invention be provide the approach of control a generation process by continue growth in the duct of the clathrate compound slurry which generated in the duct when convey petroleum and natural gas , or be generated industrially , produce naturally and make a minute amount dissolve the spherical non-\*\* protein of environmental harmony nature high type III into a water solution , in order to control the generation process of the clathrate compound used as the cause of cause lock out accident .

[Means for Solving the Problem]

[0012]

The result of having repeated research wholeheartedly about the water solution which this invention person uses for generation of a clathrate compound, the guest molecule, and the generation process of the formed clathrate compound, When making a clathrate compound form from the non-\*\* protein water solution with which it was reported that effectiveness is in generation control of ice, It becomes longer than the time of time amount (generation induction period) after reaching the generation conditions for stability of a clathrate compound phase until a crystal is generated using pure water, Moreover, even if it changed becoming later than the time of the rate which grows after a crystal is generated using pure water to the concentration of the spherical non-\*\* protein of Type III in a header and a water solution, based on the knowledge that the same result is obtained, it came to complete this invention.

[0013]

That is, this invention is the formation control approach of the clathrate compound which controls formation of this clathrate compound by a clathrate compound's facing being formed from liquids, such as water, atmosphere, and/or a solvent, and adding the spherical non-\*\* protein of Type III.

[0014]

Furthermore, in case this invention conveys and stores liquids, such as atmosphere and/or a solvent, they are transportation and the storage condition of the atmosphere and/or the liquid which are characterized by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound.

[0015]

Furthermore, this invention is the approach of preventing lock out of a duct, in the approach a duct conveys liquids, such as atmosphere and/or a solvent, by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound.

[0016]

in the approach of each above, rare gas, such as sour gases, such as hydrocarbon gas, such as methane and a propane, carbon dioxide gas, and a hydrogen sulfide, and neon, and a krypton, mentions as atmosphere -- having -- as a liquid -- organic solvents, such as fluorocarbon, such as HFC-32 and HFC-134a, a tetrahydrofuran, and an acetone, or the above -- the organic solvents and liquid hydrocarbon which generate a clathrate compound under coexistence with atmosphere, such

as a methylcyclohexane and an isopentane, are mentioned.

[0017]

Moreover, the spherical non-\*\* protein of Type III to be used has the effective concentration in the inside of a water solution at 0.01 mg/ml, and there is especially no limitation about maximum concentration.

[Effect of the Invention]

[0018]

By this invention, the clathrate compound faced being formed from liquids, such as water, atmosphere, and/or a solvent, and formation of this clathrate compound was able to be controlled by adding the spherical non-\*\* protein of Type III to these. And lock out of the duct by formation of a clathrate compound etc. was able to be prevented by applying this approach in the approach a duct conveys liquids, such as atmosphere and/or a solvent.

[Best Mode of Carrying Out the Invention]

[0019]

The approach of this invention has become from the technique which controls generation of a clathrate compound by reducing the rate a clathrate compound grows up to be, after the technique which controls generation of a clathrate compound by lengthening the time amount (generation induction period) from which a generation reaction does not occur in the bottom of the condition which can form a clathrate compound in case the guest molecule phase (the gaseous phase or liquid phase) and the water which can generate a clathrate compound are made to react, and a generation reaction occur. Non-\*\* protein here is proteinic [ which has non-\*\*\*\*\* ]. Non-\*\* protein is classified into four kinds of IV(s) according to the amino acid sequence and molecular shape from Type I (refer to drawing 1 ). In drawing 1 , in (a), (b) shows the structure (structure similar to the C-type lectin which has five disulfide bonds) of Type II, and (c) shows the structure (spherical structure which was rich in beta-sheets structure) of Type III for the structure (one alpha-helix structure) of Type I, respectively.

[0020]

Type I is molecular weight 3300-4500, and has the description that many alanines are included in an amino acid sequence. As a typical amino acid sequence, the array of the kind winter flounder origin of a flounder is mentioned (nonpatent literature 7). Molecular shape takes the Rix structure to one alpha, as shown in drawing 1 (a). Type II is molecular weight 11000-24000, and has the description that many cysteines are included in an amino acid sequence. As a typical amino acid sequence, the array of the kind sea raven origin of a sculpin is mentioned (nonpatent literature 8). As shown in drawing 1 (b), molecular shape has five disulfide bonds and takes structure similar to C-type lectin. Type III is molecular weight 6500-14000, and does not have especially the description of an amino acid sequence. As a typical amino acid sequence, the kind ocean pout origin array of milk vatch is mentioned (nonpatent literature 9). Molecular shape takes the spherical structure which was rich in beta-sheets structure, as shown in drawing 1 (c). Type IV is molecular weight 10000 and has the description that many glutamines are included in an amino acid sequence. As a typical amino acid sequence, the array of the kind longhorn sculpin origin of a sculpin is mentioned (nonpatent literature 10). Although the description of molecular shape is predicted to be the Rix bundle structure to four alpha, structural analysis is not carried out yet and clear molecular shape as shown in type I-III is not determined yet. The non-\*\* protein used by this invention is globular protein classified into Type III. The non-\*\* protein of Type III used in the example has the amino acid sequence expressed with the array number 1 of an array table. However, the effectiveness that this invention is also hung down is not limited to the amino acid sequence concerned, and is widely applied to the non-\*\* protein of Type III. Moreover, even if it calls it freezing in this invention, not ice-izing but generation of a clathrate compound is meant, and a name called non-\*\* protein (it is written as Antifreeze Protein and AFP) is usually used. In addition, in this specification, since non-\*\* protein is spherical non-\*\* protein of Type III, it is written as AFP (III) according to the context.

[0021]

As a guest molecule which can generate the clathrate compound used in this invention, rare gas, such as small molecules, such as a hydrocarbon gas which is the principal component of natural gas, such as ethane gas besides methane and a liquefied petroleum gas, carbon dioxide gas, nitrogen gas, oxygen gas, and a hydrogen sulfide, xenon gas, argon gas, and krypton gas, is mentioned. Moreover, unlike the above-mentioned guest molecule, guest molecules, such as fluorocarbon and an ammonium salt water solution, can generate a clathrate compound on ordinary pressure conditions. Although carried out here using carbon dioxide gas, generally the technique used for this invention is enacted also to a guest molecule as shown above.

[0022]

Although deionization and deaerated distilled water are usually used for the water used in this invention, even if impurities, such as a salt and a base, are contained somewhat, generally it is materialized. However, with the classes and concentration of an impurity which are contained, also when the generation equilibrium condition of a clathrate compound shifts, for a certain reason, the component ratio in the gas obtained or a clathrate compound may change.

[0023]

The conditions made to react are low temperature and high-pressure conditions from the equilibrium condition expected from the reaction of the guest molecule and pure water to be used. For example, when carbon dioxide gas is used, the equilibrium pressure force of the clathrate compound which reacts with pure water and is generated is about 1.2 MPa(s) in 273.2K. Therefore, in the experiment using this gas, it is carried out in 1.2 or more MPas. By the flow and pressure requirement, although it is arbitrary, since non-\*\* protein is hardly dissolved in ice, a temperature requirement is performed under a reaction condition with a water solution, and it is [ direction ] desirable and it is performed or more by 273.2K.

[0024]

Drawing 2 is clathrate compound generation observation equipment used by this invention. This equipment is suitable in order to be used for clathrate compound generation rate measurement by the carbon-dioxide-gas-pure-water (or salt water) system (nonpatent literature 5) and to compare the effectiveness of a non-\*\* protein water solution quantitatively. The water sample of a constant rate is paid into a high pressure vessel HV, the whole is put in into Thermostat TB, and it is made predetermined temperature. The air in HV is exhausted after that, and from Bomb B, a guest molecule sample is introduced into HV and it is made a predetermined pressure. And a setup of a thermostat is lowered and it brings to a clathrate compound generation condition. Temperature and a pressure make zero time of day which became a clathrate compound generation condition, measures temperature and a pressure with Thermocouple TC and a pressure gage PG, and records with Recorder R.

[0025]

The temperature rise of the system accompanying the visual observation from an observation window W and heat-of-formation emission performs the check of generation of a clathrate compound. Moreover, the growth rate of a clathrate compound observed the situation in a system under Microscope MS from the observation window, and measured it in analyzing the image which recorded the change on videotape with the video camera VTR, and was obtained.

[0026]

In addition, raised the temperature after the measurement experiment of a generation rate, and in a system, the clathrate compound was made to disassemble, and change of the equilibrium condition by the non-\*\* protein water solution was checked by measuring the decomposition temperature.

[0027]

The mechanism of AFP having had magnitude peculiar to the icy crystal structure, therefore having given careful consideration alternatively to the growth crystal face, and controlling growth was proposed conventionally. However, although the clathrate compound which was adapted by this

invention was the crystal of the hydrogen bond system which is an icy kind, unlike ice, the crystal structure was not able to expect the same function. However, as shown by this invention, the big growth inhibition effectiveness was acquired by the minute amount addition of 0.01 mg/ml (10-3 wt%). Since the AFP itself is the matter produced naturally, unlike the formation inhibitor compounded with chemicals, its environmental harmony nature is high. Moreover, a possibility of corroding a reaction container, a duct, etc. like NaCl also has the advantage of being few.

[0028]

Since it has the description of controlling a nucleation, without changing an equilibrium condition, growth of a clathrate compound will be remarkably controlled by stopping the driving force of crystal growth low. Moreover, it is expected that the growth rate of the film-like clathrate compound generated by the guest molecule-water interface will be controlled, and the fall of a generation rate will be observed also in the reactor system in mind and a liquid contact mold from the description that a growth rate is controlled.

[0029]

It was shown that it is possible to use as generation inhibitors, such as a clathrate compound using the ammonium salt called the methane clathrate compound which has the same crystal structure besides the system shown in the following examples of this invention from the above thing, a propane clathrate compound with the different crystal structure, many fluorocarbon clathrate compounds, and a semi- clathrate compound. Therefore, it is possible for it to be adapted in the generation controlling method by this invention about the technique of using these clathrate compounds.

[Example]

[0030]

Hereafter, an example explains this invention concretely. However, the technical range of this invention is not limited to these examples.

One drop (about 0.5 cm<sup>3</sup>) of water solution which melted AFP (III) shown in the distilled water sample which carried out deionization and degassing processing by the array number 1 by predetermined concentration is enclosed into the high-pressure reaction container HV (about 10 content volume cm<sup>3</sup>) shown in drawing 2, and is put in into Thermostat TB. In that case, the air which remained in HV opens a bulb V2, and deaerates it in vacuum pump VP. The bulb V2 after degassing is closed.

[0031]

A bulb V1 is opened after that, and after introducing a carbon-dioxide-gas sample into HV and carrying out a pressure up from Bomb B to a predetermined pressure, a bulb V1 is closed. And after checking that thermal stress has become predetermined conditions, a setup of Thermostat TB is lowered and temperature is made into predetermined temperature. After reaching the clathrate compound generation temperature in a setting pressure, it observes that a clathrate compound generates on an interface.

[0032]

Drawing 3 shows time amount t change of the temperature T to the carbon-dioxide-gas clathrate compound generation when using the water solution which melted 0.01mg (III) /of AFP ml.

Thermostat temperature was set as 263.2K and system internal pressure was set to about 5 MPa. The terminal temperature at this time was the same as about 283.2 K which is the terminal temperature of the clathrate compound called for by the pure-water-carbon dioxide gas system as a result of a decomposition experiment.

[0033]

As a result of conducting a repetition experiment, the clathrate compound was not generated during the temperature fall, but after it reached laying temperature (264.2 K) in almost all cases, it set and generated the period for a while. Therefore, DT was set to about 18 K whenever [ required for generation supercooling ]. Moreover, the induction period concerning generation was estimated at 30

- 120 minutes. In the setup with the same generation condition of the carbon-dioxide-gas inclusion hydrate when using pure water, whenever [ supercooling ] are 10K or less, and a generation induction period is less than 20 minutes (nonpatent literature 4). That is, it was shown by AFP addition that generation of a carbon-dioxide-gas clathrate compound was checked remarkably. [0034]

The experiment using the spiral non-\*\* protein classified into Type I which Zeng and others (2003) (nonpatent literature 6) performed was estimating the engine performance with the probability for a nucleation to happen, within 24 hours, when temperature was held to 273.2K. Therefore, although it is difficult to compare this example and directly, since a concentration dependency's being in non-\*\*\*\*\* and the AFP concentration used by this example are thinner than the concentration indicated by Zeng's and others paper 10 or more times, it is thought that the way of non-\*\*\*\*\* of the non-\*\* protein used by this invention won.

[0035]

Drawing 4 shows the growth rate of the carbon-dioxide-gas clathrate compound in the same experiment system. Along the axis of abscissa, DT was taken whenever [ supercooling ], and the growth rate  $v_f$  of the film-like clathrate compound for which it asked from the video image was taken along the axis of ordinate. if a drawing middle point line shows the growth rate in a pure-water-carbon dioxide gas system (nonpatent literature 4) and compares a continuous line with these results that show the dependency whenever [ supercooling / of the growth rate in a concentration 10wt% NaCl water-solution-carbon dioxide gas system ] (nonpatent literature 5) -- concentration 0.01 -- it was suggested that the growth rate in a mg/ml AFP (III) water-solution-carbon dioxide gas system has the growth suppression effectiveness equivalent to the NaCl water solution of the concentration of 3 times or more of seawater. Since it will become 10-3 wt% order if the concentration of AFP is expressed with percentage by weight, it can be said that the clathrate compound generation depressor effect of AFP used by this invention is 104 times the NaCl.

[0036]

The experiment using the spiral non-\*\* protein classified into Type I which Zeng and others (2003) (nonpatent literature 6) performed was estimating the engine performance from the specific consumption of a liquefied petroleum gas. Therefore, although it is difficult to compare this example and directly, since there being no extreme predominance in generation rate control capacity and the AFP (III) concentration used by this example are thinner than the concentration indicated by Zeng's and others paper (nonpatent literature 6) 100 or more times, it is thought that the way of the generation rate control capacity of AFP (III) used by this invention won.

[0037]

The experiment using the water solution and carbon dioxide gas which set concentration of AFP (III) to 0.1 mg/ml - 1 mg/ml as a sample was conducted like the example 1, under the same conditions, the generation induction period of a carbon-dioxide-gas clathrate compound became long compared with the pure-water-carbon dioxide gas system, and the growth rate was controlled almost like the case of AFP (III) concentration 0.01 mg/ml. Therefore, change of the effectiveness by the concentration of AFP (III) was not so large as the difference in concentration.

[Brief Description of the Drawings]

[0038]

Drawing 1 Molecular shape of each type of non-\*\* protein.

Drawing 2 Drawing showing the outline of the generation observation equipment structure used in the example.

Drawing 3 0.01 Drawing when conducting a clathrate compound generation experiment 9 times, using the water solution and carbon dioxide gas (about 5 pressure MPa) containing mg/ml AFP as a sample showing time amount  $t$  change of  $T$  whenever [ reaction container internal temperature ]. In addition, the arrow head showed the time of day when generation of a clathrate compound was checked.

[Drawing 4] 0.01 Drawing showing DT dependency whenever [ supercooling / of the clathrate compound growth rate vf when conducting a clathrate compound generation experiment, using the water solution and carbon dioxide gas (about 5 pressure MPa) containing mg/ml AFP as a sample ].

[Description of Notations]

[0039]

B: The high-pressure bomb for gas

V1, V2: Valve

HV: High-pressure reaction container

TB: Thermostat

SM: Water solution (sample)

PG: Pressure gage

TC: Thermometer

R: Recorder

VP: Vacuum pump

W: Observation window

MS: Microscope

VHS: Video camera

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## TECHNICAL FIELD

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[Field of the Invention]

[0001]

This invention relates to the approach of controlling a generation process by generating in a duct, in case petroleum and natural gas are conveyed, and dissolving the spherical non-\*\* protein of Type III into a water solution, in order to control generation of the clathrate compound used as the cause of causing lock out accident.

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## PRIOR ART

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[Background of the Invention]

[0002]

A molecule (it is called a guest molecule) and water (called a host molecule), such as hydrophobic gases, such as natural gas, and a solvent like fluorocarbon and a tetrahydrofuran, react under low-temperature high-pressure conditions, and a clathrate compound tells the high concentration far exceeding the solubility to water (or ice) the thing of the solid-state which involved the guest molecule. Although this matter was discovered at the end of the 18th century, the accident which a transportation pipe will blockade in the petrochemical plant of a high latitude area in the 1950s arose, and it attracted attention greatly as this causative agent. In order to prevent such accident after that, research has been advanced focusing on the technique which checks generation (see the nonpatent literature 1).

[0003]

A clathrate compound mainly takes two kinds of crystal structures. It is the I-beam crystal (a cubic, about 1.2nm of unit-cell length) which one reacts with methane, carbon dioxide gas, etc., and is generated, and another is II mold crystal (a cubic, about 1.7nm of unit-cell length) which reacts with a tetrahydrofuran, a liquefied petroleum gas, etc., and is generated. Although it consists of a grid

from which a water molecule makes all, an icy crystal (hexagonal,  $a=0.45\text{nm}$  of unit-cell length,  $c=0.74\text{nm}$ ) is different structure, and water intermolecular distance also differs, respectively.  
[0004]

Current serves as a candidate for research as a technique in which current and the generation control technique of a clathrate compound which the fossil fuel develops in polar regions and a large depth-sounding area gradually are old, and it is new (for example, nonpatent literature 2 reference).

Moreover, all over the submarine deposit and the permafrost layer of a polar region, it is known that the natural gas which is not only what accompanies such a fossil fuel is \*\*\*\*(ing) in the form of a clathrate compound, and the development research for developing these as a natural gas resource in recent years is started (see the nonpatent literature 3). Examination is beginning to be performed also about the technique which uses unique properties, such as high density guest molecule concealment nature which a clathrate compound furthermore has, and guest molecule selectivity at the time of generation and a decomposition reaction, and is used industrially. for example, as separation technology using a clathrate compound of mixed gas "Separation of the mixed gas using gas-hydrate and the freshening approach of seawater" (patent reference 1), the "isotope separation approach" (patent reference 2), the "separation approach of rare gas" (patent reference 3), etc. are reported. Having the point that low energy nature, small facility nature, low environmental load nature, etc. were excellent compared with technique, such as the low-temperature-separation method and membrane-separation method for having used the boiling point difference of each component in the mixed gas currently performed from the former, and an oscillating adsorption separation method, is known.

[0005]

In such ED, it is very important to control generation / decomposition behavior of a clathrate compound. As especially mentioned above, about the technique which controls generation of a clathrate compound, the application range is wide. Moreover, correlation is between the growth rate in a clathrate compound, and the guest molecule concentration in the formed clathrate compound, and in order to obtain a clathrate compound with the guest molecule concentration of a complement, it is necessary to control a generation rate.

[0006]

As a technique which controls generation of a clathrate compound, the approach using the two mainly following additives is in use. One is the approach of using the additives (for example, seawater, alcohol, etc.) shifted to an equilibrium condition of clathrate compound control-side, and it is the approach of using the additive (chemicals, such as PVP) which controls the crystal generated although other one did not change most equilibrium conditions. Although any approach is used in actual production, since the former additive does not necessarily control growth of a clathrate compound, if it becomes the equilibrium condition which the system shifted, generation of a clathrate compound cannot be controlled. Moreover, as for the latter additive, although development is furthered, effect evaluation to an environment etc. is not fully performed, but an economical problem also has current [ much ].

[0007]

Uchida et al. (nonpatent literature 4 (1999)) conducted the generation experiment of a carbon-dioxide-gas clathrate compound, and investigated the growth rate of the film-like clathrate compound generated by the pure-water-carbon-dioxide-gas interface. Consequently, it turned out that it is expressed with the function of the gap (whenever [ supercooling ] DT) from the terminal temperature of temperature in case the growth rate of a carbon-dioxide-gas clathrate compound starts generation under the pressure. Furthermore, the clathrate compound which Uchida et al. (2002) conducts the same experiment in the water solution containing NaCl, and is generated by the NaCl water-solution-carbon-dioxide-gas interface found out that growth rate depressor effect was so large that a growth rate's being slower than a pure-water system and NaCl concentration are high (nonpatent literature 5).

[0008]

As a generation control technique of the ice which is the same hydrate system crystal as a clathrate compound, the use ED of the non-\*\* protein produced naturally in recent years is active. This non-\*\* protein adheres alternatively on the icy crystal face, and it is said that it has the work which controls that crystal growth. However, the function is limited to the icy crystal structure, and is evaluated.

[0009]

Zeng and others (nonpatent literature 6) pointed out possibility that the spiral non-\*\* protein classified into Type I would control generation of II mold clathrate compounds, such as tetrahydrofuran and a liquefied petroleum gas, recently. However, effect is taken only to II mold crystal structure, and there is no report about the effectiveness to the I-beam clathrate compound crystal which reacts with methane and carbon dioxide gas which are the principal component of natural gas, and is generated.

[0010]

[Patent reference 1] JP,11-319805,A

[Patent reference 2] JP,2000-33236,A

[Patent reference 3] JP,2000-107549,A

[Nonpatent literature 1] Sloan, E.D.Jr., Clathrate Hydrates of Natural Gases 2ndEd. Revised and Expanded, Marcel Dekker Inc., 1998.

[Nonpatent literature 2] Carroll, J.J., Natural Gas Hydrates: A Guide for Engineers, Butterworth-Heinemann, 2002

[Nonpatent literature 3] Paull, C.K and Dilloin, W.P. Eds., Natural Gas Hydrates: Occurrence, Distribution, and Detection

[Nonpatent literature 4] Uchida et al. J. Crystal Growth, 204, p. 348, 1999

[Nonpatent literature 5] Uchida et al. J. Crystal Growth, 237-239, p. 383, 2002

[Nonpatent literature 6] Zeng et al Can. J. Phys., 81, p.17, 2003

[Nonpatent literature 7] Sicheri et al. Nature, 375, p. 427, 1995

[Nonpatent literature 8] Gronwald et al. Biochemistry, 37, p. 4712, 1998

[Nonpatent literature 9] Jia et al. Nature, 384, p. 285, 1996

[Nonpatent literature 10] Deng et al. Biochim. Biophys. Acta, 1388, p.305, 1998

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## EFFECT OF THE INVENTION

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[Effect of the Invention]

[0018]

By this invention, the clathrate compound faced being formed from liquids, such as water, atmosphere, and/or a solvent, and formation of this clathrate compound was able to be controlled by adding the spherical non-\*\* protein of Type III to these. And lock out of the duct by formation of a clathrate compound etc. was able to be prevented by applying this approach in the approach a duct conveys liquids, such as atmosphere and/or a solvent.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]

[0011]

this invention be provide the approach of control a generation process by continue growth in the duct of the clathrate compound slurry which generated in the duct when convey petroleum and natural gas , or be generated industrially , produce naturally and make a minute amount dissolve the spherical non-\*\* protein of environmental harmony nature high type III into a water solution , in order to control the generation process of the clathrate compound used as the cause of cause lock out accident .

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## MEANS

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### [Means for Solving the Problem]

[0012]

The result of having repeated research wholeheartedly about the water solution which this invention person uses for generation of a clathrate compound, the guest molecule, and the generation process of the formed clathrate compound, When making a clathrate compound form from the non-\*\* protein water solution with which it was reported that effectiveness is in generation control of ice, It becomes longer than the time of time amount (generation induction period) after reaching the generation conditions for stability of a clathrate compound phase until a crystal is generated using pure water, Moreover, even if it changed becoming later than the time of the rate which grows after a crystal is generated using pure water to the concentration of the spherical non-\*\* protein of Type III in a header and a water solution, based on the knowledge that the same result is obtained, it came to complete this invention.

[0013]

That is, this invention is the formation control approach of the clathrate compound which controls formation of this clathrate compound by a clathrate compound's facing being formed from liquids, such as water, atmosphere, and/or a solvent, and adding the spherical non-\*\* protein of Type III.

[0014]

Furthermore, in case this invention conveys and stores liquids, such as atmosphere and/or a solvent, they are transportation and the storage condition of the atmosphere and/or the liquid which are characterized by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound.

[0015]

Furthermore, this invention is the approach of preventing lock out of a duct, in the approach a duct conveys liquids, such as atmosphere and/or a solvent, by adding the spherical non-\*\* protein of Type III, and controlling formation of a clathrate compound.

[0016]

in the approach of each above, rare gas, such as sour gases, such as hydrocarbon gas, such as methane and a propane, carbon dioxide gas, and a hydrogen sulfide, and neon, and a krypton, mentions as atmosphere -- having -- as a liquid -- organic solvents, such as fluorocarbon, such as HFC-32 and HFC-134a, a tetrahydrofuran, and an acetone, or the above -- the organic solvents and liquid hydrocarbon which generate a clathrate compound under coexistence with atmosphere, such as a methylcyclohexane and an isopentane, are mentioned.

[0017]

Moreover, the spherical non-\*\* protein of Type III to be used has the effective concentration in the inside of a water solution at 0.01 mg/ml, and there is especially no limitation about maximum concentration.

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## EXAMPLE

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[Example]

[0030]

Hereafter, an example explains this invention concretely. However, the technical range of this invention is not limited to these examples.

One drop (about 0.5 cm<sup>3</sup>) of water solution which melted AFP (III) shown in the distilled water sample which carried out deionization and degassing processing by the array number 1 by predetermined concentration is enclosed into the high-pressure reaction container HV (about 10 content volume cm<sup>3</sup>) shown in drawing 2, and is put in into Thermostat TB. In that case, the air which remained in HV opens a bulb V2, and deaerates it in vacuum pump VP. The bulb V2 after degassing is closed.

[0031]

A bulb V1 is opened after that, and after introducing a carbon-dioxide-gas sample into HV and carrying out a pressure up from Bomb B to a predetermined pressure, a bulb V1 is closed. And after checking that thermal stress has become predetermined conditions, a setup of Thermostat TB is lowered and temperature is made into predetermined temperature. After reaching the clathrate compound generation temperature in a setting pressure, it observes that a clathrate compound generates on an interface.

[0032]

Drawing 3 shows time amount t change of the temperature T to the carbon-dioxide-gas clathrate compound generation when using the water solution which melted 0.01mg (III) /of AFP ml.

Thermostat temperature was set as 263.2K and system internal pressure was set to about 5 MPa. The terminal temperature at this time was the same as about 283.2 K which is the terminal temperature of the clathrate compound called for by the pure-water-carbon dioxide gas system as a result of a decomposition experiment.

[0033]

As a result of conducting a repetition experiment, the clathrate compound was not generated during the temperature fall, but after it reached laying temperature (264.2 K) in almost all cases, it set and generated the period for a while. Therefore, DT was set to about 18 K whenever [ required for generation supercooling ]. Moreover, the induction period concerning generation was estimated at 30 - 120 minutes. In the setup with the same generation condition of the carbon-dioxide-gas inclusion hydrate when using pure water, whenever [ supercooling ] are 10K or less, and a generation induction period is less than 20 minutes (nonpatent literature 4). That is, it was shown by AFP addition that generation of a carbon-dioxide-gas clathrate compound was checked remarkably.

[0034]

The experiment using the spiral non-\*\* protein classified into Type I which Zeng and others (2003) (nonpatent literature 6) performed was estimating the engine performance with the probability for a nucleation to happen, within 24 hours, when temperature was held to 273.2K. Therefore, although it is difficult to compare this example and directly, since a concentration dependency's being in non-\*\*\*\*\* and the AFP concentration used by this example are thinner than the concentration indicated by Zeng's and others paper 10 or more times, it is thought that the way of non-\*\*\*\*\* of the non-\*\* protein used by this invention won.

[0035]

Drawing 4 shows the growth rate of the carbon-dioxide-gas clathrate compound in the same experiment system. Along the axis of abscissa, DT was taken whenever [ supercooling ], and the growth rate vf of the film-like clathrate compound for which it asked from the video image was taken along the axis of ordinate. if a drawing middle point line shows the growth rate in a pure-

water-carbon dioxide gas system (nonpatent literature 4) and compares a continuous line with these results that show the dependency whenever [ supercooling / of the growth rate in a concentration 10wt% NaCl water-solution-carbon dioxide gas system ] (nonpatent literature 5) -- concentration 0.01 -- it was suggested that the growth rate in a mg/ml AFP (III) water-solution-carbon dioxide gas system has the growth suppression effectiveness equivalent to the NaCl water solution of the concentration of 3 times or more of seawater. Since it will become 10-3 wt% order if the concentration of AFP is expressed with percentage by weight, it can be said that the clathrate compound generation depressor effect of AFP used by this invention is 104 times the NaCl.

[0036]

The experiment using the spiral non-\*\* protein classified into Type I which Zeng and others (2003) (nonpatent literature 6) performed was estimating the engine performance from the specific consumption of a liquefied petroleum gas. Therefore, although it is difficult to compare this example and directly, since there being no extreme predominance in generation rate control capacity and the AFP (III) concentration used by this example are thinner than the concentration indicated by Zeng's and others paper (nonpatent literature 6) 100 or more times, it is thought that the way of the generation rate control capacity of AFP (III) used by this invention won.

[0037]

The experiment using the water solution and carbon dioxide gas which set concentration of AFP (III) to 0.1 mg/ml - 1 mg/ml as a sample was conducted like the example 1, under the same conditions, the generation induction period of a carbon-dioxide-gas clathrate compound became long compared with the pure-water-carbon dioxide gas system, and the growth rate was controlled almost like the case of AFP (III) concentration 0.01 mg/ml. Therefore, change of the effectiveness by the concentration of AFP (III) was not so large as the difference in concentration.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[0038]

[Drawing 1] Molecular shape of each type of non-\*\* protein.

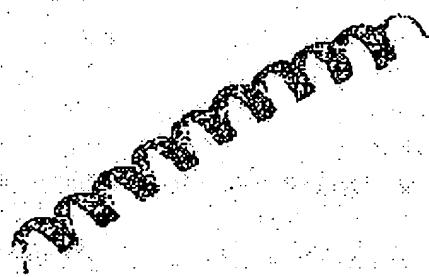
[Drawing 2] Drawing showing the outline of the generation observation equipment structure used in the example.

[Drawing 3] 0.01 Drawing when conducting a clathrate compound generation experiment 9 times, using the water solution and carbon dioxide gas (about 5 pressure MPa) containing mg/ml AFP as a sample showing time amount t change of T whenever [ reaction container internal temperature ]. In addition, the arrow head showed the time of day when generation of a clathrate compound was checked.

[Drawing 4] 0.01 Drawing showing DT dependency whenever [ supercooling / of the clathrate compound growth rate vf when conducting a clathrate compound generation experiment, using the water solution and carbon dioxide gas (about 5 pressure MPa) containing mg/ml AFP as a sample ].

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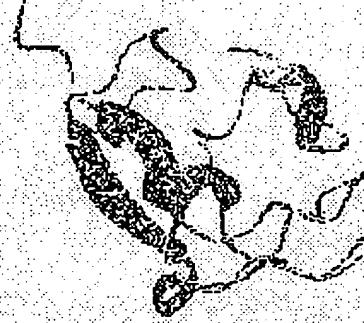
(3) タイプ I AFP

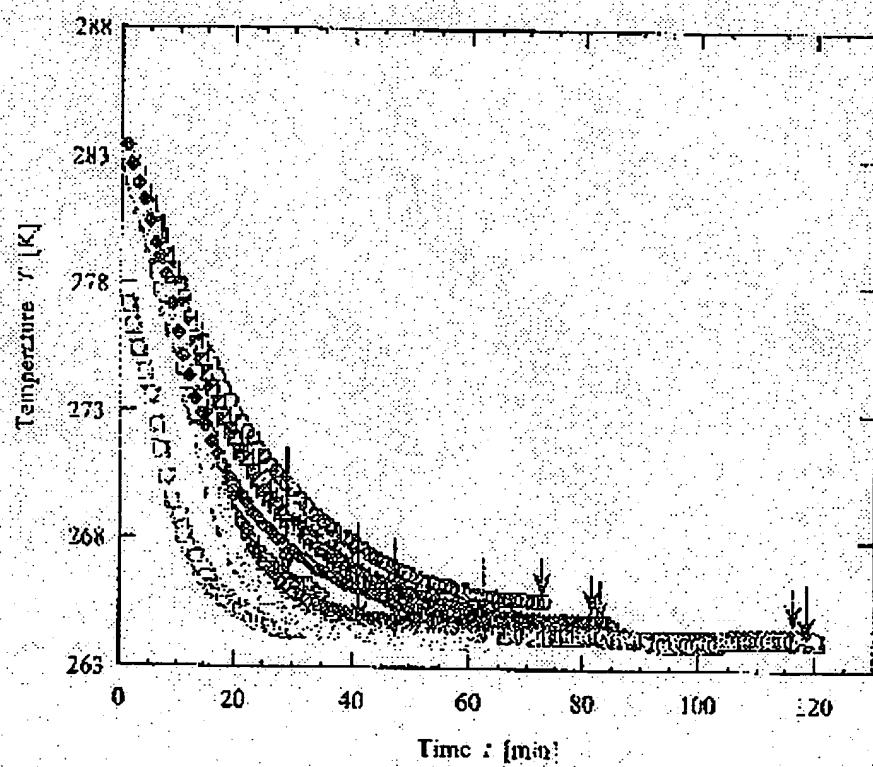
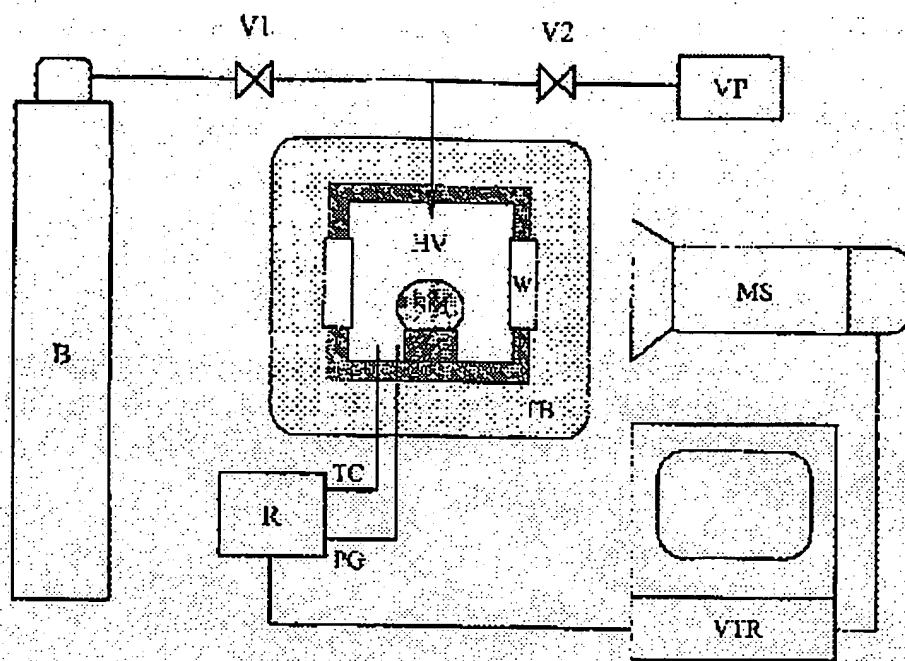


(3) タイプ II AFP



(3) タイプ III AFP





## SEQUENCE LISTING

<110> National Institute of Advanced Industrial Science and Technology (AIST)

<120> Formation process controlling of clathrate hydrates with adding antifreeze protein

<130> 323H03014

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Val Asn Arg Ala Val Pro Leu Gly Thr Thr Leu Met Pro Asp Met Val Lys Asn Tyr Glu Asp Gly Thr  
Thr Ser Pro Gly Leu Lys